

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of an application for a German Patent

with the file reference 102 15 010.9

filed on 05 April 2002

in the name of Covion Organic Semiconductors GmbH, Frankfurt am Main, Germany,

and in the matter of an application for an United States Patent.

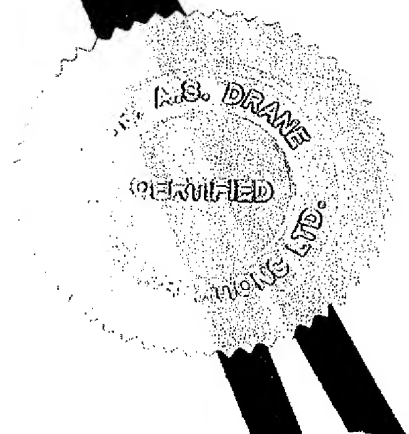
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1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the German and English languages and am a competent translator thereof.
3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 28th day of August 2008



Dr. Ashwood Stephen Drane



FEDERAL REPUBLIC OF GERMANY



Priority certificate regarding the filing of a patent application

File reference: 102 15 010.9

Date of filing: 05 April 2002

Applicant/proprietor: Covion Organic Semiconductors GmbH,
Frankfurt am Main/DE

Title: Rhodium and iridium complexes

IPC: C 07 F, H 01 L, C 09 K

**The attached pages are a correct and accurate reproduction of the
original documents of this patent application.**

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Munich, 6 June 2003
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On behalf of
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Description

Rhodium and iridium complexes

Organometallic compounds - especially compounds of the d^8 metals - will in the near future be used as functional components as active components (= functional materials) in a number of applications of different types which can be ascribed to the electronics industry in the broadest sense.

In the case of organic electroluminescent devices based on organic components (general description of the structure cf. US-A-4,539,507 and US-A-5,151,629) or individual components thereof, the organic light-emitting diodes (OLEDs), the market introduction has already taken place, as confirmed by the available car radios with an "organic display" from Pioneer. Further products of this type are just about to be introduced. Nevertheless, significant improvements are still necessary here in order to make these displays a true competitor to the liquid-crystal displays (LCDs) which currently dominate the market, or to surpass them.

A development in this respect which has emerged in the last two years is the use of organometallic complexes which exhibit phosphorescence instead of fluorescence [M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, Applied Physics Letters, **1999**, 75, 4-6].

For theoretical spin-statistical reasons, an up to four-fold energy and power efficiency is possible using organometallic compounds as phosphorescent emitters.

Whether this new development will succeed is highly dependent on whether it is possible to find corresponding device compositions which are also able to implement these advantages (triplet emission = phosphorescence compared with singlet emission = fluorescence) in OLEDs. Essential conditions for practical use which may be mentioned here are, in particular, a long operating lifetime, high stability to temperature stresses and a low use and operating voltage in order to facilitate mobile applications.

In addition, there must be efficient chemical access to the corresponding organometallic compounds. Of particular interest here are organorhodium and iridium compounds. It is of crucial importance in these, in particular taking into account the

price of rhodium and iridium, that efficient access to corresponding derivatives is facilitated.

To date, two designs of OLEDs which have phosphorescent emitters as colouring components have been described in the literature.

The first type (type 1) typically has the following layer structure [M. E. Thompson et al., Proceedings of SPIE, 31.07 - 02.08.2000, San Diego, USA, Volume 4105, page 119 - 124]:

1. Outer plate = substrate (usually glass or plastic films).
2. Transparent anode (usually indium tin oxide, ITO).
3. Hole-transport layer: usually based on triarylamine derivatives.
4. Electron-transport and emission layer: this layer consists of an electron-transport material which is doped with the phosphorescent emitter.
5. Electron-transport layer: in the majority of cases based on aluminium tris-8-hydroxyquinoxalinate (AlQ_3).
6. Cathode: metals, metal combinations or metal alloys having a low work function, for example Al/Li, are generally used here.

The second type (type 2) typically has the following layer structure [T. Tsutsui et al. Jpn. J. Appl. Phys., **1999**, 38, L 1502 - L 1504]:

1. Outer plate = substrate (usually glass or plastic films).
2. Transparent anode (usually indium tin oxide, ITO).
3. Hole-transport layer: usually based on triarylamine derivatives.
4. Matrix and emission layer: this layer consists of a matrix material, usually based on triarylamine derivatives, which is doped with the phosphorescent emitter.
5. Electron-transport/hole-blocking layer: usually based on nitrogen heterocycles.
6. Electron-transport layer: in the majority of cases based on aluminium tris-8-hydroxyquinoxalinate (AlQ_3).
7. Cathode: metals, metal combinations or metal alloys having a low work function, for example Al, are generally used here.

It is also possible to couple the light out of a thin transparent cathode. These devices are correspondingly structured (depending on the application), provided with con-

tacts and are finally also hermetically sealed since the lifetime of such devices is generally drastically reduced in the presence of water and/or oxygen.

The characteristic data of the OLEDs described above exhibit two weak points: Firstly, the phosphorescent emitters described to date based on tris-ortho-metallated iridium complexes are not suitable for the construction of efficient blue and in particular dark-blue OLEDs, since none of the known phosphorescent emitters emits in the dark blue, i.e. at an emission wavelength λ_{\max} of less than 465 nm. However, dark-blue phosphorescent emitters are of crucial importance, in particular, for the production of full-colour displays, for which the primary colours RED-GREEN-BLUE must be available.

Secondly, it can be seen from the efficiency/luminance curves that the efficiency drops rapidly with increasing luminance. This means that the high luminances necessary in practice can only be achieved via high power consumption. However, high power consumptions require high battery performances of portable equipment (mobile phones, laptops, etc.). In addition, the high power consumption, which is for the most part converted into heat, can result in thermal damage to the display.

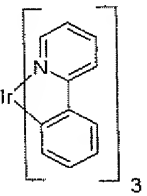
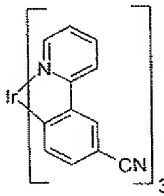
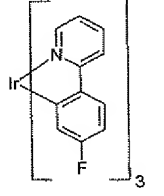
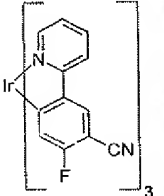
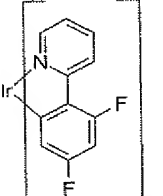
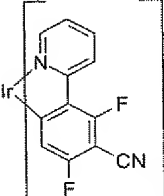
These deficiencies in the prior art give rise to the following objects. Firstly, there is a need for the production of, for example, blue - in particular dark-blue - triplet emitters, secondly it is necessary to provide triplet emitters which have extremely linear efficiency/luminance curves, even at high luminances.

5'-Mono-, 5',5"-di- and 5',5'',5'''-triscyano-functionalised tris-ortho-metallated organorhodium and organoiridium compounds - as per compounds (I/Ia) or (II/IIa) - to which the present invention relates, will be central key building blocks for the production of highly efficient triplet emitters. Crucial material properties, such as the wavelength of the phosphorescence emission, i.e. the colour, the phosphorescence quantum yield and the redox and temperature stability of the emitters, to mention but a few properties by way of example, can be adjusted via a corresponding cyano functionalisation.

The class of 5'-mono-, 5',5''-di- and 5',5'',5'''-tricyano-functionalised tris-ortho-metallated organorhodium and organoiridium compounds - as per compounds (I/Ia) or (II/IIa)- is novel and has not been described to date in the literature, but the efficient preparation and availability thereof as pure substances is of major importance for a number of electro-optical applications.

Surprisingly, it has been found that the wavelength of the phosphorescence emission of a triplet emitter, i.e. the "colour" of the emitted light, experiences a hypsochromic shift on introduction of cyano functions into the 5'-, 5''- or 5'''-position (see Table 1).

Table 1: Influence of the 5-substituents on absorption and phosphorescence

Reference to Example 1	Example 1	Reference to Example 2	Example 2	Reference to Example 3	Example 3
					
$\lambda_{\text{max, emission}}$	$\lambda_{\text{max, emission}}$	$\lambda_{\text{max, emission}}$	$\lambda_{\text{max, emission}}$	$\lambda_{\text{max, emission}}$	$\lambda_{\text{max, emission}}$
535 nm	515 nm	514 nm	464 nm	470 nm	442 nm
green	dark green	dark green	pale blue	cyan	dark blue

$\lambda_{\text{max, emission}}$

Maximum of the electroluminescence band

Besides the direct use of 5'-mono-, 5',5''-di- and 5',5'',5'''-tricyano-functionalised tris-ortho-metallated organorhodium and organoiridium compounds (as per compounds (I/Ia) or (II/IIa)), to which the present invention relates, in light-emitting devices, these will also be central key building blocks for the production of highly efficient triplet emitters, since the cyano function can be converted into a multiplicity of functions

with the aid of standard methods described in the literature. Starting from the said structures, literature-known methods open up access to alcohols, amines, aldehydes and carboxylic acids and derivatives thereof, but also to heterocycles, such as azoles, diazoles, triazoles, oxazolines, oxazoles, oxadiazoles, thiazoles, thiodiazoles, etc., and benzo-fused derivatives thereof.

5'-Mono-, 5',5''-di- and 5',5'',5'''-tricyano tris-ortho-metallated organorhodium and organoiridium compounds and processes for the preparation thereof are novel and have not been described to date in the literature. This applies, in particular, to the cyanation of halogenated, aromatic ligands - *which are bonded to the metal centre* - i.e. cyanation on the metal complex by replacement of the halogen function with the cyano function. However, the efficient preparation and availability of these cyano compounds as pure substances is of major importance for various electro-optical applications.

Surprisingly, it has been found that the novel cyano-substituted organometallic compounds (I/Ia) or (II/IIa) are obtained reproducibly - in accordance with scheme 1 and 2 - starting from the 5'-mono-, 5',5''-di- and 5',5'',5'''-trihalo-substituted tris-ortho-metallated organorhodium or organoiridium compounds (III) or (IV) [preparation as described in the unpublished DE 10109027 A], i.e. starting from *organometallic aryl halides* - by stoichiometric reaction with a transition-metal cyanide or by catalytic reaction with a transition-metal cyanide, optionally in the presence of a transition metal, a transition-metal compound and a phosphorus-containing additive, and with suitable choice of the reaction parameters, such as reaction temperature, reaction medium, concentration and reaction times, in approximately 90 - 98% yield, without the use of chromatographic purification methods, if necessary after recrystallisation, in purities of > 99% according to NMR or HPLC (see Examples 1-6).

The process described above is distinguished, in particular, by three properties:

Firstly, the selective 5'-mono-, 5',5''-di- and 5',5'',5'''-tricyanation of coordinatively bonded aryl halides - i.e. of *organometallic aryl halides* - is unexpected and unknown in this form.

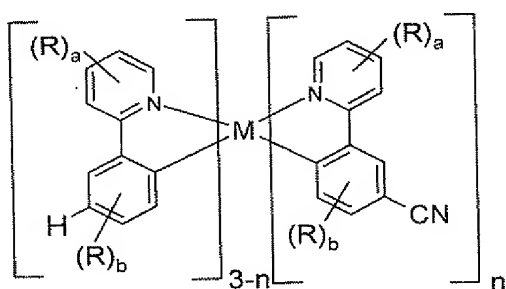
Secondly, the high conversion achieved, which is reflected in the reproducibly very good yields of isolated product, is unexpected and unique for the cyanation of coordinatively bonded aryl halides.

Thirdly, the resultant compounds are obtained in very good purities of > 99% according to NMR or HPLC, without complex chromatographic purification, if necessary after recrystallisation. This is essential for use in opto-electronic components or for use as intermediates for the preparation of corresponding compounds.

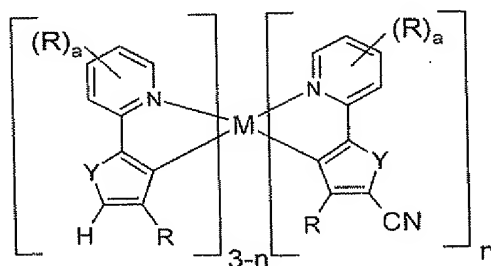
As outlined above, the compounds according to the invention have not been described before and are thus novel.

The present invention thus relates to the compounds (I) and (II), as shown in scheme 1,

Scheme 1:



Compounds (I)



Compounds (II)

where the symbols and indices have the following meaning:

M Rh, Ir;

Y O, S, Se;

R is, identically or differently on each occurrence, H, F, Cl, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent CH₂ groups may be replaced by -O-, -S-, -NR¹-, or -CONR²- and in which one or more H atoms may be replaced by F, or an aryl or heteroaryl group having 4 to

14 C atoms, which may be substituted by one or more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, together may in turn form a further mono- or polycyclic ring system;

R^1, R^2 are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

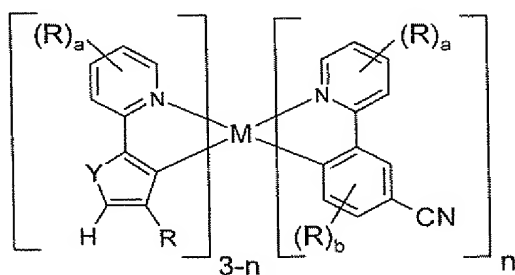
a is 0, 1, 2, 3 or 4, preferably 0, 1 or 2, particularly preferably 0 or 1;

b is 0, 1, 2 or 3, preferably 0 or 1;

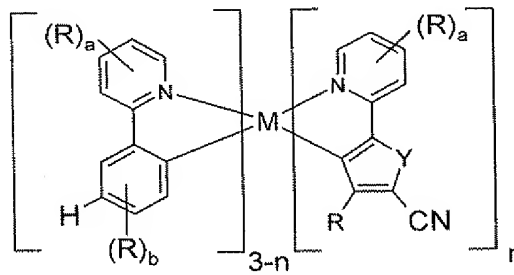
n is 1, 2 or 3

A further embodiment of the invention are Rh or Ir complexes of this type which simultaneously have ligands of the type as in compounds (I) and those of compounds (II), i.e. mixed ligand systems. These are described by the formulae (Ia) and (IIa) - as shown in scheme 2:

Scheme 2:



Compounds(Ia)

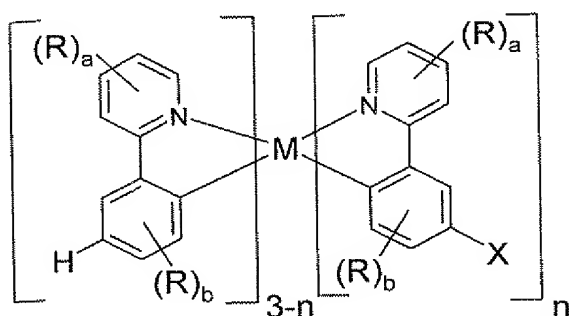


Compounds (IIa)

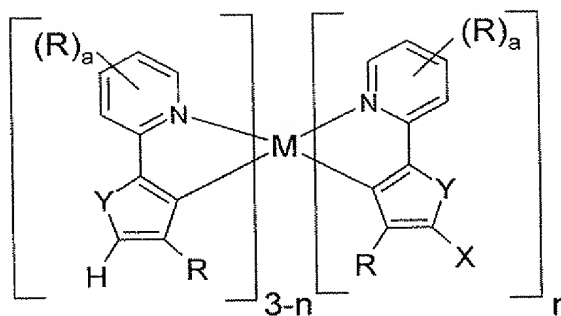
where the symbols and indices have the meanings indicated under the formulae (I) and (II).

Preference is given to compounds (Ia), (II) and (IIa) according to the invention in which the symbol $Y = O, S$.

The present invention furthermore relates to a process for the preparation of the compounds (I) or (II) by reaction of the compounds (III) or (IV) respectively



Compound (III)



Compound (IV)

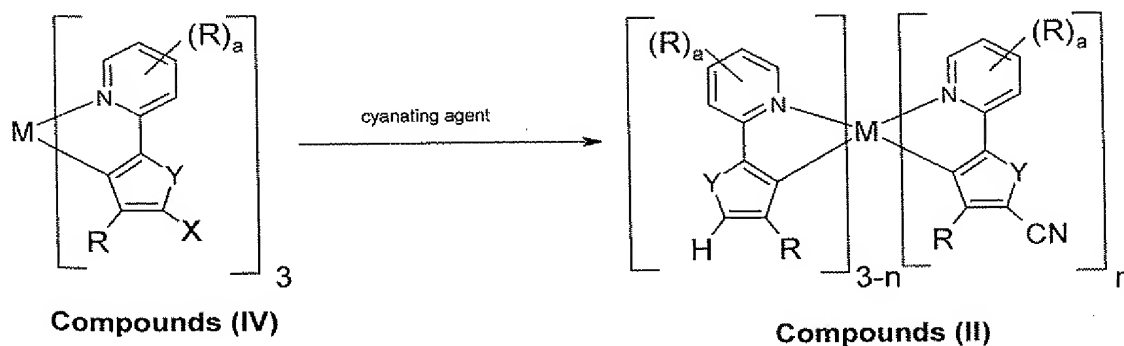
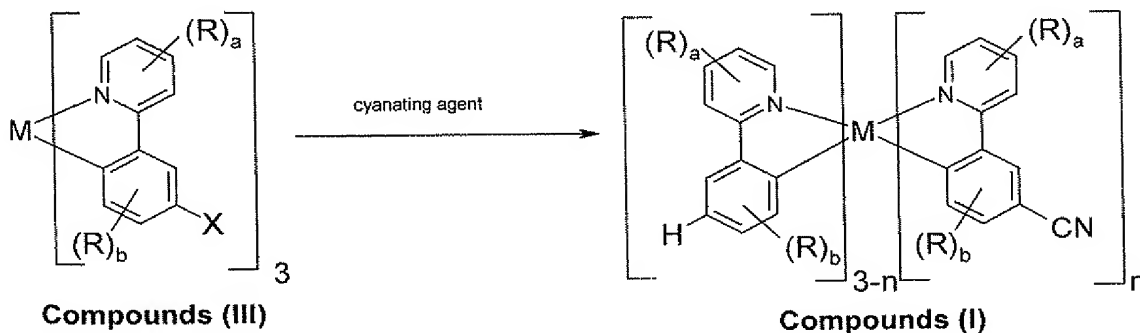
in which:

X is Cl, Br or I,

and M, the radicals R and the indices a, and b and n have the meanings indicated under compound (I) and (II) respectively, with a cyanating agent.

The process according to the invention is explained by scheme 2:

Scheme 2:



Cyanide sources according to the invention are compounds which contain the cyanide ion in ionic or coordinatively bonded form, for example sodium, potassium, magnesium, tetraethylammonium, tetrabutylammonium, nickel(II), copper(I), silver(I), zinc(II) cyanide or sodium and potassium dicyanocuprate(I), tetracyanocuprate(II), tetracyanozincate(II), tetracyanonickelate(II), tetracyanopalladate(II).

Preferred cyanating agents are firstly transition-metal cyanides, for example copper(I) cyanide or nickel(II) cyanide. These cyanating agents are referred to below as cyanating agents (1)..

A further preferred cyanating agent is zinc(II) cyanide in the presence of zinc, and in the presence of nickel or palladium or a nickel or palladium compound and optionally of a phosphorus-containing additive. These cyanating agents are referred to below as cyanating agents (2).

Nickel according to the invention or nickel compounds for the cyanating agents (2) are, for example, elemental nickel, nickel sponge, nickel on kieselguhr, nickel on aluminium oxide, nickel on silica, nickel on carbon, nickel(II) acetate, nickel(II) acetylacetonate, nickel(II) chloride, bromide, iodide, addition compounds of the NiL_2X_2 type, where X corresponds to chlorine, bromine, iodine and L corresponds to a neutral ligand, such as, for example, ammonia, acetonitrile, propionitrile, benzonitrile, or nickel(II) nitrate, nickel(II) sulfate, nickel(II) oxalate, biscyclooctadienyl-nickel(0).

Palladium according to the invention or palladium compounds for the cyanating agents (2) are, for example, elemental palladium, palladium sponge, palladium black, palladium on active carbon, palladium on aluminium oxide, palladium on silica, palladium on alkali or alkaline earth metal carbonates, such as sodium carbonate, potassium carbonate, calcium carbonate, strontium carbonate or barium carbonate, palladium on strontium sulfate or barium sulfate, or palladium compounds, such as, for example, palladium(II) acetate, palladium(II) trifluoroacetate, palladium(II) propionate, palladium(II) acetylacetonate, palladium(II) chloride, bromide, iodide, addition compounds of the PdL_2X_2 type, where X corresponds to

chlorine, bromine, iodine and L corresponds to a neutral ligand, such as, for example, ammonia, acetonitrile, propionitrile, benzonitrile, cyclooctadiene, or palladium(II) nitrate, palladium(II) sulfate, palladium(II) tetraamine acetate, palladium(II) tetrakis-(acetonitrile) tetrafluoroborate, sodium tetracyanopalladate, potassium tetracyanopalladate, tetrakis(triphenylphosphino)palladium(0) and tris(dibenzylideneacetone)-dipalladium(0).

In accordance with the invention, the phosphorus-containing additive used in the cyanating agents (2) is a phosphine.

Phosphine ligands according to the invention for the cyanating agents (2) are from the group of the triarylphosphines, diarylalkylphosphines, arylalkylphosphines, trialkylphosphines, trihetarylphosphines, dihetarylalkylphosphines, hetarylalkylphosphines, where the substituents on the phosphorus may be identical or different, chiral or achiral, where one or more of the substituents may link the phosphorus groups of a number of phosphines and where some of these links may also be one or more metal atoms, for example triphenylphosphine, tri-*o*-tolylphosphine, trimesitylphosphine, tri-*o*-anisylphosphine, tri(2,4,6-trimethoxyphenyl)phosphine, *tert*-butyldi-*o*-tolylphosphine, di-*tert*-butyl-*o*-tolylphosphine, dicyclohexyl-2-biphenylphosphine, di-*tert*-butyl-2-biphenylphosphine, triethylphosphine, triisopropylphosphine, tricyclohexylphosphine, tri-*tert*-butylphosphine, tri-*tert*-pentylphosphine, bis(di-*tert*-butylphosphino)methane, 1,1'-bis(di-*tert*-butylphosphino)ferrocene.

The molar ratio according to the invention of the cyanating agents (1) and (2) to the compounds (III) or (IV) is $1\ n : 1$ to $10\ n : 1$, preferably $1.5\ n : 1$ to $3\ n : 1$.

The molar ratio according to the invention of zinc(II) cyanide to zinc in the cyanating agents (2) is $1 : 0.1$ to $1 : 0.001$, preferably $1 : 0.05$ to $1 : 0.005$.

The molar ratio according to the invention of nickel, a nickel compound, palladium or a palladium compound to the compounds (III) or (IV) is $0.1\ n : 1$ to $0.00001\ n : 1$.

The molar ratio according to the invention of the phosphorus-containing additive to nickel, a nickel compound, palladium or a palladium compound is 0.5 : 1 to 1000 : 1.

Reaction media according to the invention are dipolar aprotic solvents, for example nitriles, such as acetonitrile, propionitrile or benzonitrile, or N,N-dialkylamides, such as dimethylformamide, dimethylacetamide or N-methylpyrrolidinone, sulfoxides, such as dimethyl sulfoxide, sulfones, such as dimethyl sulfone, or sulfolane.

In accordance with the invention, the reaction is carried out in the temperature range from 60°C to 200°C, preferably at 80°C to 170°C, particularly preferably at 100°C to 160°C.

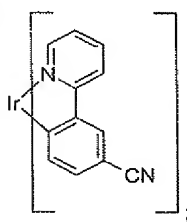
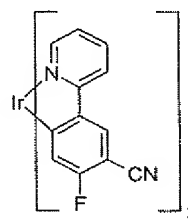
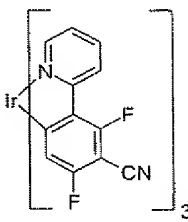
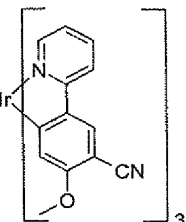
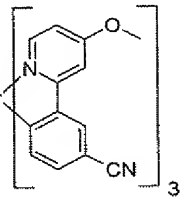
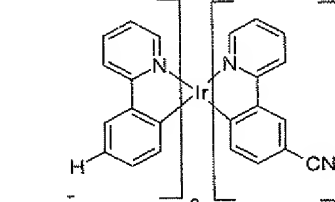
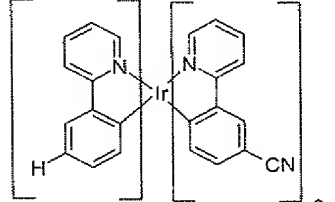
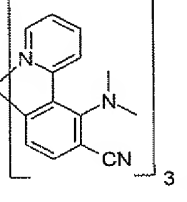
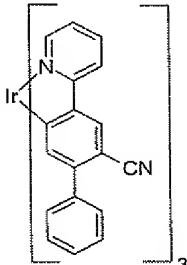
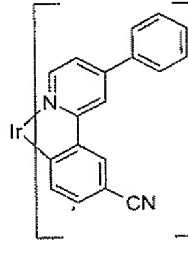
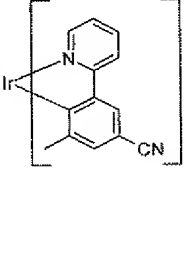
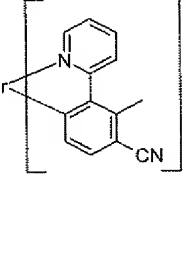
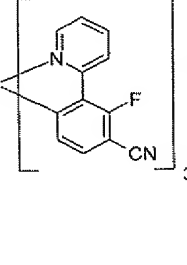
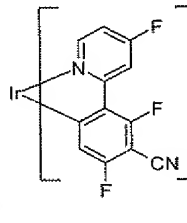
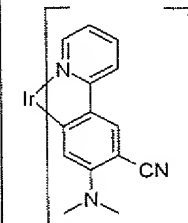
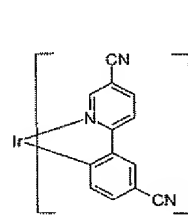
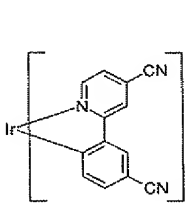
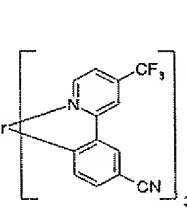
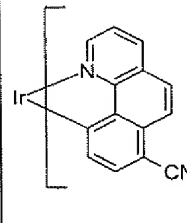
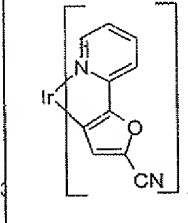
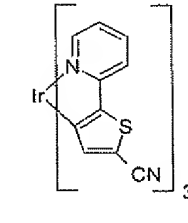
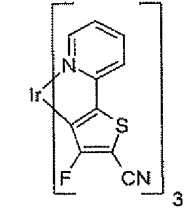
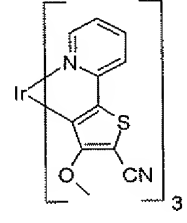
In accordance with the invention, the concentration of the rhodium-containing or iridium-containing starting materials - compounds (III) or compounds (IV) respectively - is in the range from 0.0005 mol/l to 2 mol/l, particularly preferably in the range from 0.002 mol/l to 0.1 mol/l.

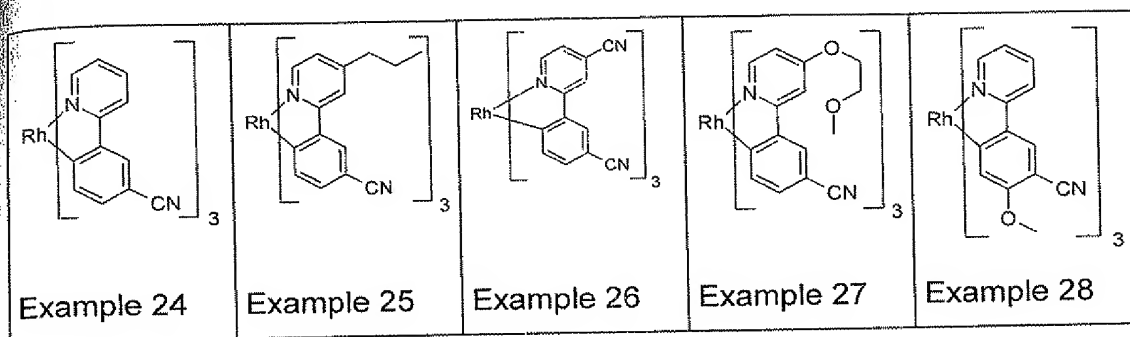
In accordance with the invention, the rhodium-containing or iridium-containing starting materials can be dissolved or suspended in the reaction medium.

In accordance with the invention, the reaction is carried out over the course of 1 hour to 100 hours, preferably over the course of 1 h to 60 h.

In accordance with the invention, the reaction can be carried out with addition of inert grinding media, such as, for example, ceramic, glass or metal balls or Pall or Raschig rings.

The examples of compounds (I) and (II) shown below, inter alia, can be prepared using the synthetic methods explained here.

				
Example 1	Example 2	Example 3	Example 4	Example 7
				
Example 5	Example 6	Example 8		
				
Example 9	Example 10	Example 11	Example 12	Example 13
				
Example 14	Example 15	Example 16	Example 17	Example 18
				
Example 19	Example 20	Example 21	Example 22	Example 23



The iridium and rhodium compounds according to the invention can be used in electronic components, such as organic light-emitting diodes (OLEDs), organic integrated circuits (O-ICs), organic field-effect transistors (OFETs), organic thin-film transistors (OTFTs), organic solar cells (O-SCs), organic laser diodes (O-lasers), organic coloured filters for liquid-crystal displays or organic photo receptors. The present invention likewise relates to these.

The present invention is explained in greater detail by the following examples, without wishing it to be restricted thereto. The person skilled in the art will be able to prepare further complexes according to the invention or use the process according to the invention from the descriptions without inventive step.

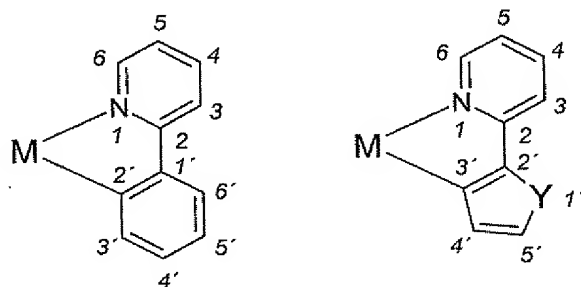
1. Synthesis of symmetrically and asymmetrically functionalised tris-ortho-metallated organorhodium or organoiridium compounds:

The following syntheses were carried out - unless indicated otherwise - in dried solvents under a protective-gas atmosphere. The starting materials were purchased from ALDRICH [sodium cyanide, copper(I) cyanide, zinc(II) cyanide, zinc, tetrakis-(triphenylphosphino)palladium(0), N-methylpyrrolidinone (NMP)]. *fac*-Tris[2-(2-pyridinyl-κN)(5-bromophenyl)-κC]iridium(III), *fac*-tris[2-(2-pyridinyl-κN)((4-fluoro)-5-(bromo)phenyl)-κC]iridium(III), *fac*-tris[2-(2-pyridinyl-κN)((4,6-fluoro)-5-(bromo)phenyl)-κC]iridium(III) and *fac*-tris[2-(2-pyridinyl-κN)((4-methoxy)-5-(bromo)phenyl)-κC]iridium(III) was prepared as described in the unpublished application DE 10109027.7.

The assignment of the ¹H-NMR signals was in some cases confirmed by H-H-COSY spectra, that of the ¹³C{¹H}-NMR signals in each case via DEPT-135 spectra.

Numbering scheme for the assignment of the $^1\text{H-NMR}$ signals [in accordance with: C. Coudret, S. Frayse, J.-P. Launay, Chem. Commun., **1998**, 663-664]:

Scheme 3:



Example 1: *fac*-Tris[2-(2-pyridinyl- κ N)(5-cyanophenyl)- κ C]iridium(III)

Method A: Use of a cyanating agent 1

A suspension of 8.915 g (10 mmol) of *fac*-tris[2-(2-pyridinyl- κ N)(5-bromophenyl)- κ C]iridium(III) and 5.374 g (60 mmol) of copper(I) cyanide in 150 ml of NMP was heated at 145°C for 60 h. After cooling, the brown solution was poured in one portion into a vigorously stirred solution at 50°C of 7.4 g of sodium cyanide in a mixture of 500 ml of water and 500 ml of ethanol, and the mixture was stirred at 50°C for 2 h. The microcrystalline precipitate was subsequently filtered off (P4). The microcrystalline yellow precipitate was washed three times with in each case 100 ml of a solution of 7.4 g of sodium cyanide in a mixture of 500 ml of water and 500 ml of ethanol, three times with in each case 100 ml of a mixture of ethanol and water (1:1, v v) and finally twice with 100 ml of ethanol and then dried in vacuo (60°C, 10^{-4} mbar). The yield - with a purity of > 99.0% according to $^1\text{H-NMR}$ - was 7.094 - 7.236 g, corresponding to 97.2 - 99.1%.

Method B: Use of a cyanating agent 2

347 mg (0.3 mmol) were added to a suspension of 8.915 g (10 mmol) of *fac*-tris[2-(2-pyridinyl- κ N)(5-bromophenyl)- κ C]iridium(III), 4.403 g (37.5 mmol) of zinc(II) cyanide and 98 mg (1.5 mmol) of zinc dust in 150 ml of NMP, and the mixture was heated at 100°C for 60 h.

Work-up analogously to method A. The yield - with a purity of > 99.0% according to $^1\text{H-NMR}$ - was 6.877 - 6.956 g, corresponding to 94.2 - 95.3%.

^1H NMR (DMSO- d_6): [ppm] = 8.41 (d, 1 H, $^3J_{\text{HH}} = 8.4$ Hz, H6), 8.31 (s, 1 H, H6'), 7.94 (br. dd, 1 H, $^3J_{\text{HH}} = 8.4$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, H5), 7.54 (d, 1 H, $^3J_{\text{HH}} = 5.4$ Hz, H3), 7.30 (br. dd, 1 H, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{HH}} = 5.4$ Hz, H4), 7.11 (d, 1 H, $^3J_{\text{HH}} = 8.0$ Hz, H4'), 6.74 (d, 1 H, $^3J_{\text{HH}} = 8.0$ Hz, H3').

$^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6): [ppm] = 168.5 (q), 163.0 (q), 147.3 (t), 145.6 (q), 138.3 (t), 136.7 (t), 131.7 (t), 127.3 (t), 124.6 (t), 120.5 (t), 120.4 (q), 102.8 (q).

**Example 2: *fac*-Tris[2-(2-pyridinyl- κ N)(4-fluoro-5-cyanophenyl)- κ C]-
iridium(III)**

Method A: Use of a cyanating agent 1

A suspension of 9.455 g (10 mmol) of *fac*-tris[2-(2-pyridinyl- κ N)(4-fluoro-5-bromophenyl)- κ C]iridium(III) and 5.374 g (60 mmol) of copper(I) cyanide in 200 ml of NMP was heated at 160°C for 60 h.

Work-up see Example 1, method A. The yield - with a purity of > 99.0% according to

^1H -NMR - was 7.638 - 7.710 g, corresponding to 97.5- 98.4%.

^1H NMR (DMSO- d_6): [ppm] = 8.46 (d, 1 H, $^4J_{\text{HF}} = 6.4$ Hz, H6'), 8.40 (br. d, 1 H, $^3J_{\text{HH}} = 8.3$ Hz, H6), 8.01 (br. dd, 1 H, $^3J_{\text{HH}} = 8.3$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, H5), 7.48 (br. d, 1 H, $^3J_{\text{HH}} = 5.6$ Hz, H3), 7.33 (br. dd, 1 H, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{HH}} = 5.6$ Hz, H4), 6.37 (d, 1 H, $^3J_{\text{HF}} = 10.05$ Hz, H3').

**Example 3: *fac*-Tris[2-(2-pyridinyl- κ N)(4,6-difluoro-5-cyanophenyl)- κ C]-
iridium(III)**

Method A: Use of a cyanating agent 1

A suspension of 9.635 g (10 mmol) of *fac*-tris[2-(2-pyridinyl- κ N)(4,6-fluoro-5-bromophenyl)- κ C]iridium(III) and 5.374 g (60 mmol) of copper(I) cyanide in 200 ml of NMP was heated at 160°C for 60 h.

Work-up see Example 1, method A. The yield - with a purity of > 99.0% according to

^1H -NMR - was 7.638 - 7.710 g, corresponding to 97.5- 98.4%.

^1H NMR (DMSO- d_6): [ppm] = 8.46 (br. d, 1 H, $^3J_{\text{HH}} = 8.2$ Hz, H6), 8.21 (br. dd, 1 H, $^3J_{\text{HH}} = 8.2$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, H5), 7.47 (br. d, 1 H, $^3J_{\text{HH}} = 5.8$ Hz, H3), 7.30 (br. dd, 1 H, $^3J_{\text{HH}} = 7.0$ Hz, $^3J_{\text{HH}} = 5.8$ Hz, H4), 6.32 (dd, 1 H, $^3J_{\text{HF}} = 10.05$ Hz, $^5J_{\text{HF}} = 1.35$ Hz, H3').

**Example 4: *fac*-Tris[2-(2-pyridinyl- κ N)(4-methoxy-5-cyanophenyl)- κ C]-
iridium(III)**

Method A: Use of a cyanating agent 1

A suspension of 9.816 g (10 mmol) of *fac*-tris[2-(2-pyridinyl- κ N)(4-methoxy-5-bromophenyl)- κ C]iridium(III) and 5.374 g (60 mmol) of copper(I) cyanide in 200 ml of NMP was heated at 145°C for 60 h.

Work-up see Example 1, method A. The yield - with a purity of > 99.0% according to ¹H-NMR - was 7.935 - 8.030 g, corresponding to 96.7 - 97.9%.

¹HNMR (DMSO-d₆): [ppm] = 8.27 (d, 1 H, ³J_{HH} = 8.4 Hz, H6), 8.21 (s, 1 H, H6'), 7.94 (br. dd, 1 H, ³J_{HH} = 8.4 Hz, ³J_{HH} = 6.7 Hz, H5), 7.54 (d, 1 H, ³J_{HH} = 5.1 Hz, H3), 7.30 (br. dd, 1 H, ³J_{HH} = 6.7 Hz, ³J_{HH} = 5.1 Hz, H4), 6.41 (s, 1 H, H3'), 3.48 (s, 3 H, CH₃).

2. Production and characterisation of organic electroluminescent devices comprising compounds according to the invention.

LEDs were produced by the general process outlined below. This naturally had to be adapted in individual cases to the particular circumstances (for example layer thickness variation in order to achieve optimum efficiency or colour).

General process for the production of OLEDs:

After the ITO-coated substrates (for example glass support, PET film) have been cut to the correct size, they are cleaned in a number of cleaning steps in an ultrasound bath (for example soap solution, Millipore water, isopropanol).

For drying, they are blown off with an N₂ gun and stored in a desiccator. Before vapour deposition with the organic layers, they are treated for about 20 minutes using an ozone plasma unit. It may be advisable to use a polymeric hole-injection layer as the first organic layer. This is generally a conjugated, conductive polymer, such as, for example, a polyaniline derivative (PANI) or a polythiophene derivative (for example PEDOT, BAYTRON PTM from BAYER). This is then applied by spin coating.

The organic layers are applied successively by vapour deposition in a high-vacuum unit. The layer thickness of the respective layer and the vapour-deposition rate is monitored and adjusted via a quartz resonator.

It is also possible - as described above - for individual layers to consist of more than one compound, i.e. generally for a host material to be doped with a guest material.

This is achieved by co-evaporation from two or more sources.

Electrodes are then applied to the organic layers. This is generally carried out by thermal evaporation (Balzer BA360 or Pfeiffer PL S 500). The transparent ITO electrode is subsequently contacted as anode and the metal electrode (for example Ca, Yb, Ba-Al) as cathode, and the device parameters are determined.

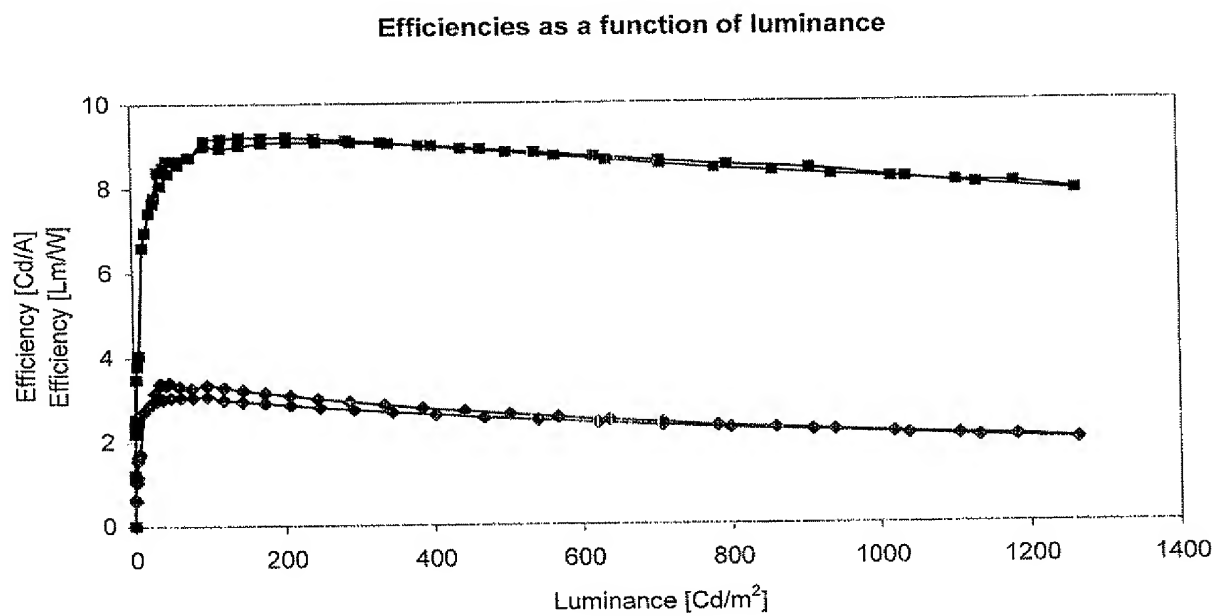
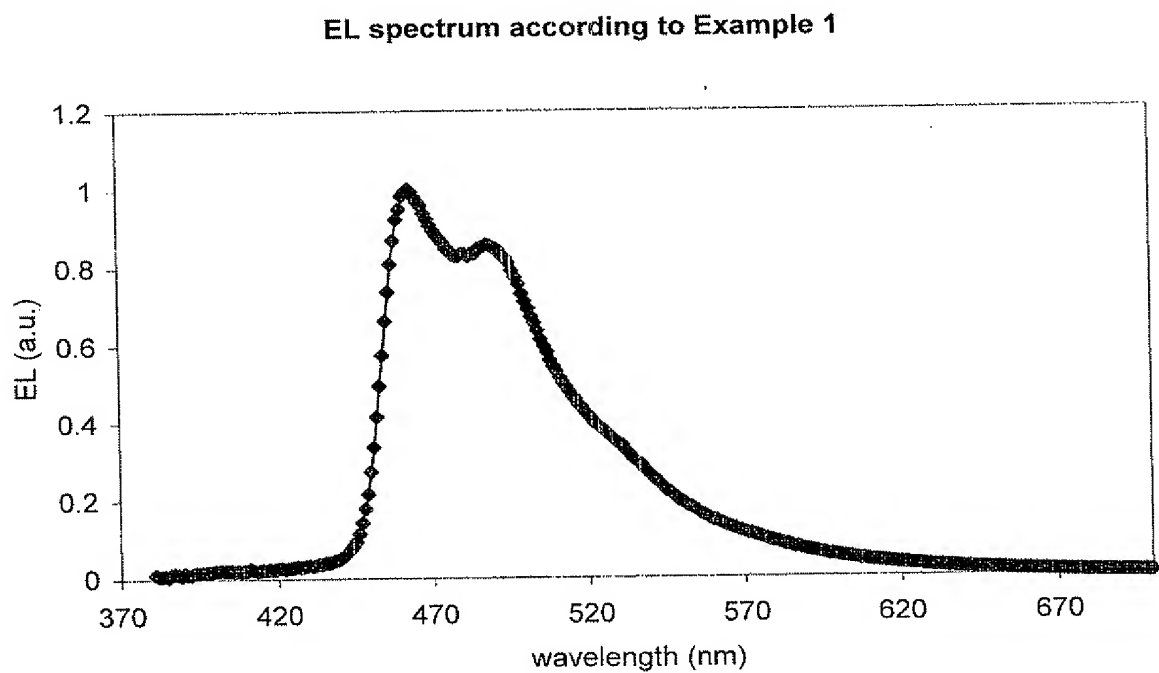
Example 5:

A blue-emitting OLED having the following structure was produced analogously to the above-mentioned general process:

PEDOT	20 nm (spin-coated from water; PEDOT purchased from BAYER AG; poly[3,4-ethylenedioxy-2,5-thiophene])
MTDATA	20 nm (vapour-deposited; MTDATA purchased from SynTec; tris-4,4',4''-(3-methylphenylphenylamino)triphenylamine)
S-TAD	20 nm (vapour-deposited; S-TAD prepared as described in WO99/12888; 2,2',7,7'-tetrakis(diphenylamino)spirobifluorene)
CPB	20 nm (vapour-deposited; CPB purchased from ALDRICH and purified further, finally sublimed twice; 4,4'-bis(N-carbazolyl)biphenyl) doped with 6%
Triplet emitter	<i>fac-tris[2-(2-pyridinyl-κN)(4-fluoro-5-cyanophenyl)-κC]iridium(III)</i> <i>compare Example 3</i>
BCP	8 nm (vapour-deposited; BCP purchased from ABCR, used as supplied; 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)
AlQ ₃	20 nm (vapour-deposited; AlQ ₃ purchased from SynTec; tris-(quinoxalinato)aluminium(III))
Yb	150 nm as cathode

This unoptimised OLED was characterised by standard methods; the EL spectrum is shown in Figure 1. Besides the colour, an enormous advantage of these OLEDs is the flatness of the efficiency curve, which means that very high efficiencies are still achieved even at very high luminances (for example 10,000 Cd/m²). This is of crucial importance in particular for use in passive-matrix-driven displays.

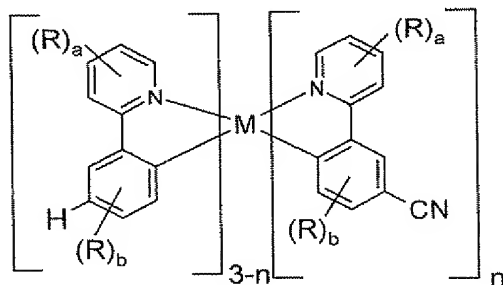
Figure 1: Characteristic data of the OLED according to Example 1



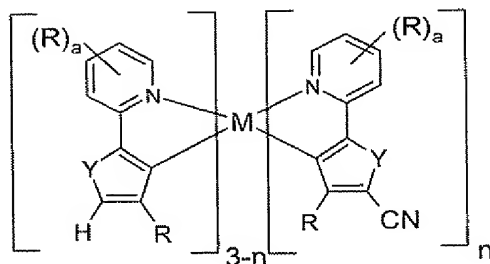
Patent Claims:

2002/CVG 011

1. Compounds of the formula (I) and (II)



Compounds(I)



Compounds (II)

where the symbols and indices have the following meaning:

M Rh, Ir;

Y O, S, Se;

R is, identically or differently on each occurrence, H, F, Cl, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 C atoms, in which one or more non-adjacent CH₂ groups may be replaced by -O-, -S-, -NR¹-, or -CONR²- and in which one or more H atoms may be replaced by F, or an aryl or heteroaryl group having 4 to 14 C atoms, which may be substituted by one or more non-aromatic radicals R; where a plurality of substituents R, both on the same ring and also on the two different rings, together may in turn form a further mono- or polycyclic ring system;

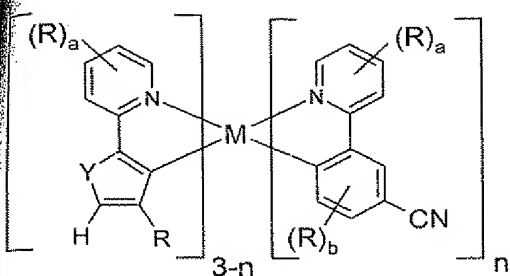
R¹, R² are, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

a is 0, 1, 2, 3 or 4, preferably 0, 1 or 2, particularly preferably 0 or 1;

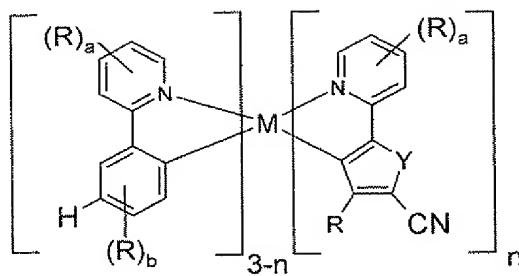
b is 0, 1, 2 or 3, preferably 0 or 1;

n is 1, 2 or 3

2. Compounds of the formula (Ia) and (IIa)



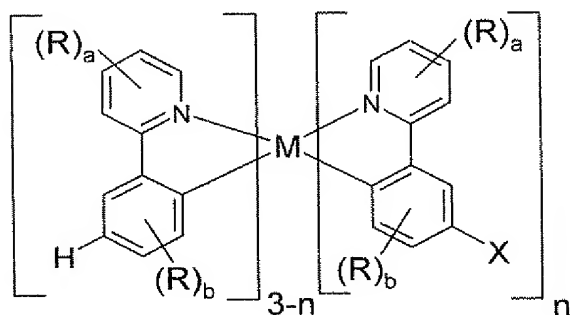
Compounds (Ia)



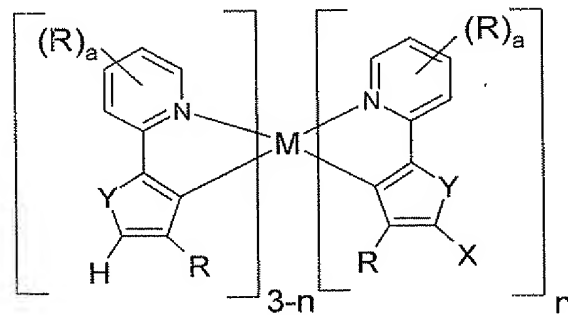
Compounds (IIa)

where the symbols and indices have the meanings as in Claim 1.

3. Process for the preparation of the compounds according to Claim 1, by reaction of the compounds (III) or (IV)



Compound (III)



Compound (IV)

in which

X is Cl, Br or I and in which M and the radicals and indices Z, R, a, and b have the meanings indicated in Claim 1, with cyanating agents.

4. Process according to Claim 3, characterised in that the cyanating agents used are systems having cyanide sources which contain the cyanide ion in ionic or coordinatively bonded form.

5. Process according to Claim 3 and / or 4, characterised in that the cyanating agents used are copper(I) cyanide or nickel(II) cyanide.

6. Process according to one or more of Claims 3 to 5, characterised in that the cyanating agent used is zinc(II) cyanide in the presence of zinc and in the presence of nickel or palladium or a nickel or palladium compound and optionally of a phosphorus-containing additive.

7. Process according to one or more of Claims 3 to 6, characterised in that the molar ratio of the cyanating agents (1) and (2) to the compounds (III) or (IV) is $1n : 1$ to $10n : 1$, preferably $1.5n : 1$ to $3n : 1$.

8. Process according to one or more of Claims 3, 6 and 7, characterised in that the molar ratio of zinc(II) cyanide to zinc in the cyanating agents (2) is $1 : 0.1$ to $1 : 0.001$, preferably $1 : 0.05$ to $1 : 0.005$.

9. Process according to one or more of Claims 3 and 6 to 8, characterised in that the ratio of nickel, a nickel compound, palladium or a palladium compound to the compounds (III) or (IV) is $0.1n : 1$ to $0.00001n : 1$.

10. Process according to one or more of Claims 3 and 6 to 9, characterised in that the ratio of the phosphorus-containing additive to nickel, a nickel compound, palladium or a palladium compound is $0.5 : 1$ to $1000 : 1$.

11. Electronic component comprising at least one compound according to one or more of Claims 1 and / or 2.

Abstract

2002/CVG 011

Rhodium and iridium complexes

The present invention describes novel organometallic compounds which are phosphorescence emitters. Compounds of this type can be employed as active components (= functional materials) in a number of applications of different types which can be ascribed to the electronics industry in the broadest sense.

The compounds according to the invention are described by the formulae (I), (Ia), (II) and (IIa).